Principles of Polymer Chemistry

2nd Edition

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$$\Delta F_{el} = kT[1.5(\alpha^2 - 1) - \ln \alpha^2]$$

where the parameter α can be expressed in terms of thermodynamic quantities:

$$\alpha^5 - \alpha^3 = 2 C_m \psi_1 (1 - \Theta/T) M^{0.5}$$

In the above equation C_m represents a combination of molecular and numerical constants. Based on the above equation, at Θ temperature $\alpha = 1$. It has been stated that the Flory-Krigbaum treatment must be treated with some reservations, because it predicts that α increases without limit with increasing molecular weight.[31,46]

1.7. Molecular Weights and Molecular Weight Determinations

Among synthetic polymers, the process of polymer formation, whether by a chain propagating reaction or through a step-growth one, is governed by random events. The result is that the chains vary in length. A polymeric material cannot, therefore, be characterized by a single molecular weight, but instead it must be represented by a statistical average.[31] This average can be expressed in several ways. One way is to present the average as a *number average* It is the sum of all the molecular weights of the individual molecules present divided by their total number. Each molecule contributes equally to the average. It can be obtained by averaging the measurements of all the colligative properties. If the total number of moles is N_i, the sum of these molecules present can be expressed as, ΣN_i . The total weight ω of a sample is similarly the sum of the weights of all the molecular species present,

$$\omega = \Sigma \omega_i = \Sigma M_i N_i$$

By dividing the total weight of the molecules by their total number we have the *number average* molecular weight,

$$\bar{M}_n = \frac{\omega}{\Sigma N_i} = \frac{\Sigma M_i N_i}{\Sigma N_i}$$

Another way to express the molecular weight average is as a *weight average.* Each molecule in such an average contributes according to the ratio of its particular weight to that of the total ,

$$\bar{M}_w = \frac{\Sigma M_i^2 N_i}{\Sigma M_i N_i}$$

The above can be illustrated quite readily by imagining that a sample consists of five molecules of molecular weights of 2,4,6,8, and 10, respectively. To calculate the number average molecular weight all the weights of the individual molecules are added. The sum is then divided by the total number of molecules in the sample (in this case 5) :

$$\bar{M}_n = 2/5 + 4/5 + 6/5 + 8/5 + 10/5 = 6$$

To calculate the weight average molecular weight of the above sample, the squares of each individual weight are divided by the total sum of molecular weights, that in this case is 30:

$$\bar{M}_w = 2^2/30 + 4^2/30 + 6^2/30 + 8^2/30 + 10^2/30 = 7.33$$

$\bar{M}_w$ is more sensitive to the higher molecular weight species, while M_n is sensitive to the lower ones. This can be seen by imagining that equal weights of two different sizes of molecules are combined, M_1 = 10,000 and M_2 = 100,000. The combination would consist of ten molecules of M_1 and one molecule of M_2. The weight average molecular weight of this mixture is 55,000 while the number average molecular weight is only 18,200. If, however, the mixture consists of an equal number of these molecules, then the weight average molecular weight is 92,000 and the number average molecular weight is 55,000.

In solutions of polymers the viscosities are more affected by the long chains than by the short ones. A correlation of the viscosity of the solution to the size of the chains or to molecular weight of the solute, allows an expression of a *viscosity average* molecular weight:

$$\bar{M}_\eta = (\sum M_i^{\beta+1} N_i / \sum M_i N_i)^{1/\beta}$$

where, β is a constant. When $\beta = 1$, then $\bar{M}\eta = \bar{M}_w$. In fact, the value of $\bar{M}\eta$ is usually within 20% of M_w.

Solution viscosities of linear polymers relate empirically to their molecular weights. This is used in various ways to designate the size of polymers. The efflux time t of a polymer solution through a capillary is measured. This is related to the efflux time t_o of the pure solvent. Typical viscometers, like those designed by Ubbelohde, Cannon-Fenske, and other similar ones, are used in a constant temperature bath. Following relationships are used:

Name	Symbol	Definitions
1. Relative viscosity	η_{rel}	$\eta/\eta_o = t/t_o$
2. Specific viscosity	η_{sp}	$(\eta-\eta_o)/\eta_o = \eta_{rel} - 1 \propto (t-t_o)/t_o$
3. Reduced viscosity	η_{red}	$\eta_{sp}/C = \eta_{rel}^{-1}/C$
4. Inherent viscosity	η_i	$\ln\eta_{rel}/C$
5. Intrinsic viscosity	$[\eta]_{c\to0}$	$(\eta_{sp}/C)_{c=0} = (\eta_i)_{c=0}$

To determine the intrinsic viscosity, both inherent and reduced viscosities are plotted against concentration (C) on the same graph paper and extrapolated to zero. If the intercepts coincide then this is taken as the intrinsic viscosity. If they do not, then the two intercepts are averaged. The relationship of intrinsic viscosity to molecular weight is expressed by the Mark-Houwink-Sakurada equation[7]:

$$[\eta]_{c=0} = K \bar{M}_\eta^{\alpha}$$

where, K and a are constants. Various capillary viscometers are available commercially. One common model is illustrated in Figure 1.6.

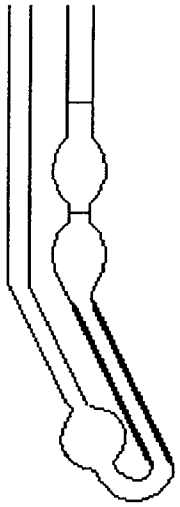

Figure 1.6. Cannon-Fenske capillary viscometer

The logarithms of intrinsic viscosities of fractionated samples are plotted against log M_w or log M_n. The constants a and K of the Mark-Houwink-Sakurada equation are the intercept and the slope, respectively, of that plot. Except for the lower molecular weight samples, the plots are linear for linear polymers. Many values of K and a for different linear polymers appear in the literature.[23] When all macromolecular species are of the same size, the number average molecular weight is equal to the weight average molecular weight. On the other hand, the greater the distribution of molecular sizes, the greater is the disparity between averages. The ratio of this disparity, M_w/M_n is a measure of *polymeric dispersity*. A *monodisperse* polymer has:

$$M_w/M_n = 1$$

In all synthetic polymers and in many naturally occurring ones the weight average molecular weight is greater than the number average molecular weight. Such polymers are *polydisperse*.

Two samples of the same polymer equal in weight average molecular weight may exhibit different physical properties, if they differ in the molecular weight distributions. Many effects of the molecular weight distribution on such properties as elongation, relaxation modulus, tensile strength, and tenacity were reported.[2]

The physical properties of polymers are also related to their molecular weights. Melt viscosity, hot strength, solvent resistance and overall toughness increase with molecular size. Table 1.4 illustrates the effect of molecular weights (size) upon physical properties of polyethylene.[32] The determinations of molecular weights of polymers rely, in most cases, upon physical methods. In some special ones, however, when the molecular weights are fairly low, chemical techniques can be used. Such determinations are limited to only those macromolecules that possess only one functional group that is located at the end of the chain ends. In place of the functional group, there may be a heteroatom. In that case, an elemental analysis might be sufficient to determine the molecular weight. If there is a functional group, however, a reaction of that group allows calculating the molecular weight. Molecular weights above 25,000 make chemical approaches impractical. In chemical determination each molecule contributes equally to the total. This is, therefore, a number average molecular weight determination

There are various physical methods available today. The more prominent ones are ebullioscopy, cryoscopy, osmotic pressure measurements, light scattering, ultracentrifugation, and gel permeation chromatography (also called size exclusion

chromatography). All these determinations are carried out on solutions of the polymers. Also, all, except gel permeation chromatography, require that the results of the measurements be extrapolated to zero concentrations to fulfill the requirements of theory. The laws that govern the various relationships used in these determinations apply only to ideal solutions. Only when there is acomplete absence of chain entanglement and no interaction between solute and solvent is the ideality of such solutions approached. A brief discussion of some techniques used for molecular weight determination follows. *Ebullioscopy*, or boiling point elevation, as well as *cryoscopy*, or freezing point depression, are well-known methods.They are the same as those used in determining molecular weights of small molecules. The limitation to using both methods with macromolecules is that ΔT_b and ΔT_f become increasingly smaller as the molecular sizes increase. The methods are limited, therefore, to the capabilities of the temperature sensing devices to detect very small differences in temperature. This places the upper limits for such determinations to somewhere between 40,000 to 50,000. The thermodynamic relationships for these determinations are:

$$[\Delta T_{b/c}]_{c\to 0} = RT^2/\rho \Delta H_b M$$
boiling point rise

$$[\Delta T_{f/c}]_{c\to 0} = RT^2/\rho \Delta H_f M$$
freezing point depression

The above two determinations, because each molecule contributes equally to the properties of the solutions, yield number average molecular weights.

A method that is useful for higher molecular weight polymers is based on *osmotic pressure measurements*. It can be applied to polymers that range in molecular weights from 20,000 to 500,000 (some claim 1,000,000 and higher). The method is based on van't Hoff's law. When a pure solvent is placed on one side of a semi-permeable membrane and a solution on the other, pressure develops from the pure solvent side. This pressure is due to a tendency by the liquids to equilibrate the concentrations. It is inversely proportional to the size of the solute molecules. The relationship is as follow:

$$M_n = RT/(\pi/C)_{C=0} + A_2C$$

where, π is the osmotic pressure, C is the concentration, T is temperature, and R is the gas constant, A_2 is a measure of interaction between the solvent and the polymer (second viral coefficient).

Table 1.4. Properties of Low Density Polyethylene[32,33]

DP	Mol. Weight	Soft.Temp. (°C)	Phys. State,_25°C
1	28	-169 (mp)	Gas
6	170	-12 (mp)	Liquid
35	1000	37	Grease
140	4000	93	Wax
250	7000	98	Hard wax
430	12000	104	Plastic
750	21000	110	Plastic
1350	38000	112	Plastic

A *static* capillary osmometer is illustrated in Fig. 1.7. Rather than rely on the liquid to rise in the capillary on the side of the solution in response to osmotic pressure, as is done in the static method, a *dynamic equilibrium* method can be used. Here a counterpressure is applied to maintain equal levels of the liquid in both capillaries and prevents flow of the solvent. Different types of dynamic membrane osmometers are available commercially.

The results obtained from either method must still be extrapolated to zero concentration for van't Hoff's law to apply. Such extrapolation is illustrated in Fig. 1.8. Because all molecules contribute equally to the total pressure, osmotic pressure measurements yield the number average molecular weight.

Light scattering measurement is a technique that is used for determining the weight average molecular weight. When light passes through a solvent a part of the energy of that light is lost due to absorption, conversion to heat, and scattering. The scattering in pure liquids is attributable to differences in densities that result from finite nonhomogeneities in the distribution of molecules within adjacent areas. Additional scattering results from a presence of a solute in the liquid. The intensity or amplitude of that additional scattering depends upon concentration, the size, and the polarizability of the solute plus some other factors. The refractive index of pure solvent and a solution is also dependent upon the amplitude of vibration. The turbidity that arises from scattering is related to concentration:

$$\text{turbidity, } \tau = Hc\overline{M}_w$$

$$H = 32\pi^3 n_o^2 (dn/dc)^2 \div 3\lambda^4 N_o$$

where, n_o is the refractive index of the solvent, n is the refractive index of the solution, λ is the wavelength of the incident light, N_o is Avogadro's number, and c is the concentration. The *dn/dc* relationship is obtained by measuring the slope of the refractive index as a function of concentration. It is constant for a given polymer, solvent, and temperature and is called the *specific refractive increment.*

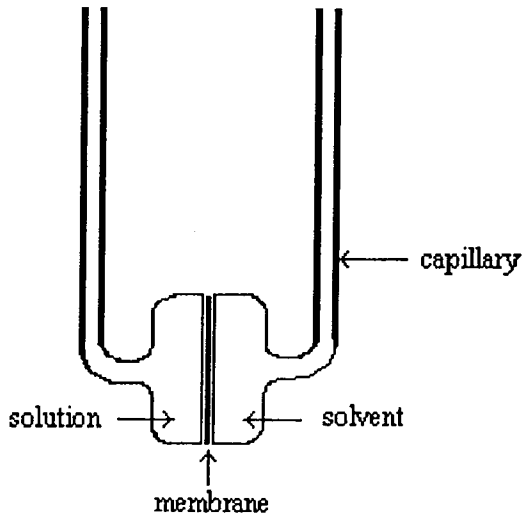

FIGURE 1.7. Membrane Osmometer

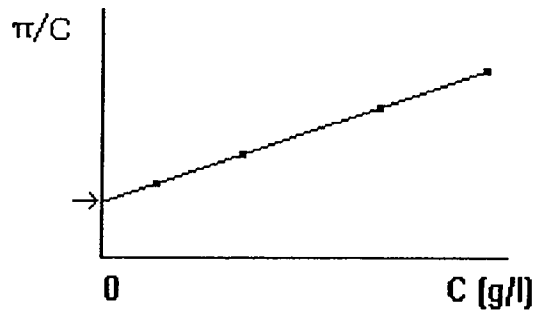

Figure 1.8. Extrapolation to zero concentration

Because scattering varies with different angles from the main beam of light, the results must be extrapolated to zero concentration and zero angle of scattering. This is done simultaneously by a method developed by Zimm. A typical Zimm plot is illustrated in Fig. 1.9.

A popular technique for determining molecular weights and molecular weight distributions is *gel permeation chromatography*. It is also called size exclusion chromatography.[42,43] The procedure allows one to determine M_w, M_n, M_z, and the molecular weight distribution in one operation. It is a form of HPLC that separates molecules according to their hydrodynamic volumes or their effective sizes in solutions. The separation takes place on one or more columns packed with a porous support. It results from retention of the polymer molecules by the pores of the packing as the solvent elutes the material through the columns. It was postulated in the past that the separation is due to smaller molecules diffusing into all the pores while the larger ones only into some of the pores. The largest molecules were thought to diffuse into none of the pores and pass only through the interstitial volumes. As a result, polymer molecules of different sizes travel different distances down the column. This means that the molecules of the largest size (highest molecular weight) are eluted first because they fit into the least number of pores. The smallest molecules, on the other hand, are eluted last because they enter the greatest number of pores and travel the longest path. The rest fall in between. The process, however, is more complex than the above postulated picture. It has not yet been fully explained. It was found, for instance, that different gels display an almost identical course in the relation of dependence of V_R (retention volume) to the molecular weight. Yet study of the pores of different gels show varying cumulative distributions of the inner volumes. This means that there is no simple function correlating the volume and/or the size of the separated molecules with the size and distribution of the pores.[42] Also, the shape of the pores that can be inferred from the ratio of the area and volume of the inner pores is very important[43]. Different models were proposed to explain the separation phenomenon. These were reviewed thoroughly in the literature.[44] They are beyond the scope of this book.

As indicated above, the volume of the liquid that corresponds to a solute eluting from the columns is called the retention volume or elution volume (V_R). It is related to the physical parameters of the column as follows:

$$VR = V_o + KV_I$$

where, V_O = the interstitial volume of the column(s)

K = the distribution coefficient

V_I = the internal solvent volume inside the pores

The total volume of the columns is V_T that is equal to the sum of V_O and V_I. The retention volume can then be expressed as follows :

$$V_R = V_O(1+K) + KV_T$$

From the earlier statement it should be clear that polymer fractionation by gel permeation chromatography depends upon the spaces the polymer molecules occupy

in solution. By measuring, experimentally, the molecular weights of polymer molecules as they are being eluted one obtains the molecular weight distribution. To accomplish this, however, one must have a chromatograph equipped with dual detectors. One must detect the presence of polymer molecules in the effluent. The other one must measure their molecular weights. Such detectors might be, for instance, a refractive index detector and a low angle laser light scattering photogoniometer to find the absolute value of M.

Many molecular weight measurements, however, are done on chromatographs equipped with only one detector that monitors the presence of the solute in the effluent. The equipment must, therefore, be calibrated prior to use. The relationship of the ordinate of the chromatogram, commonly represented by F(V), must be related to the molecular weight. This relationship varies with the polymer type and structure. There are three methods for calibrating the chromatograph. The first, and most popular one, makes use of narrow molecular weight distribution reference standards. The second one is based upon a polydisperse reference material. The third one assumes that the separation is determined by molecular size. All three methods require that an experimentally established calibration curve of the relationship between the molecular size of the polymer in solution and the molecular weight be developed. A chromatogram is obtained first from every standard sample. A plot is then prepared from the logarithms of the average weights against the peak retention volumes (V_R). The values of V_R are measured from the points of injection to the appearances of the maximum values of the chromatograms. The resultant curve may appear as shown in Fig. 1.10. Above M_1 and below M_4 there is no effective fractionation because of total exclusion in the first place and total permeation in the second case. These are the limits of separation by the packing material.

To date the standard samples of narrow molecular weight distribution polymers that are available commercially are mainly polystyrenes. These samples have polydispersity indexes that are close to unity and are available over a wide range of molecular weights. For determining molecular weights of polymers other than polystyrene, however, the molecular weights obtained from these samples would be only approximations. Sometimes they could be in error. To overcome this difficulty a *universal calibration method* is used.

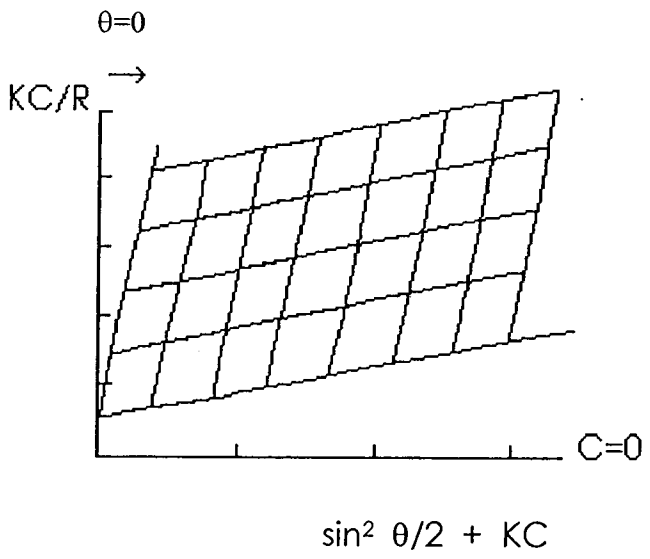

Figure 1. 9. A typical Zimm plot.

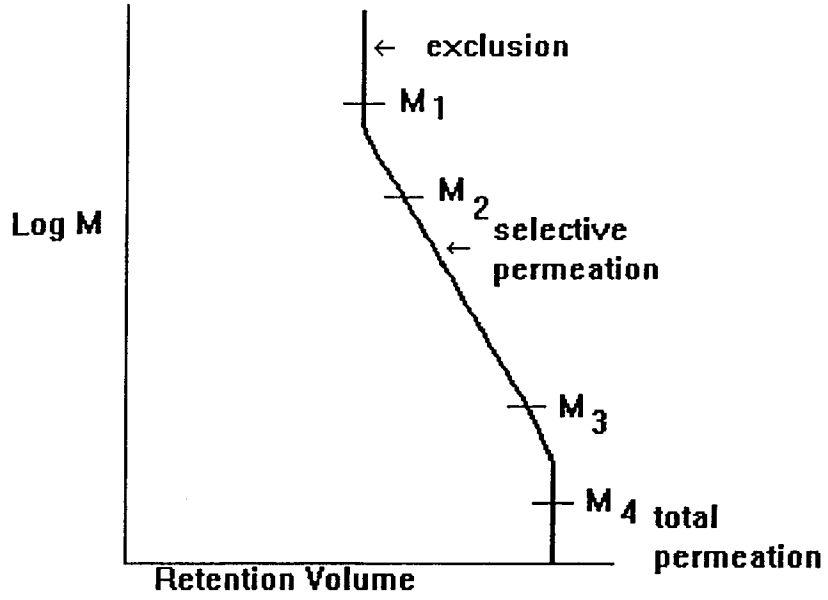

Figure 1.10. Molecular weight calibration curve

The basis for universal calibration is the observation[42] that the multiplication products of intrinsic viscosities and molecular weights are independent of the polymer types. Thus, $[\eta]M$ is the *universal calibration parameter*. As a result, a plot of log ($[\eta]M$) versus elution volume yields a curve that is applicable for many polymers. The log ($[\eta]M$) *for a given column (or columns), temperature, and elution volume* may be considered a constant for all polymers.

Numerous materials have been used for packing the columns. Semirigid crosslinked polystyrene beads are available commercially. They are used quite frequently. Porous beads of glass or silica are also available. In addition, commercial gel permeation equipment is usually provided with automatic sample injection and fraction collection features. The favorites are refractive index and ultraviolet light spectroscopic detectors. Some infrared spectroscopic detectors are also in use. Commercially available instruments also contain pumps for high-pressure rapid flow and may also be equipped with a microcomputer to assist in data treatment. Also, there is usually a plotter in the equipment to plot the detector response as the samples are eluted through the column or columns. A typical chromatogram is illustrated in Figure 1.11 . When polydisperse samples are analyzed, quantitative procedures consist of digitizing the chromatograms by drawing vertical lines at equally spaced retention volumes. These can be every 2.5 or 5.0 ml. of volumes. The resultant artificial fractions are characterized by their heights h_i, their solute concentrations C_i, and by the area they occupy within the curve A_i. The cumulative polymer weight values is calculated according to:

$$I(V) = 1/A_T \Sigma A_i$$

After conversion of the retention volumes V_i into molecular weights
(using the primary calibration curve), the molecular weights, M_w, M_n, and M_z can be calculated:

$$M_n = \Sigma h_I/(\Sigma h_I/M_i); \qquad M_w = \Sigma h_iM_I/\Sigma h_i; \qquad M_z = \Sigma h_iM_i^2/\Sigma h_iM_I$$

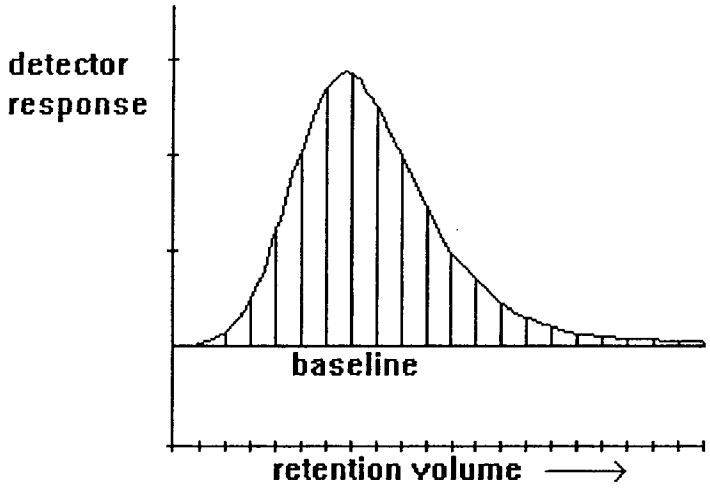

Figure 1.11. A typical digitized gel permeation chromatogram

If the chromatogram is not equipped with a microcomputer for data treatment, one can easily determine results on any available PC. Programs for data treatment have been written in various computer languages. One such program, written in Pascal language, is offered to students who may wish to practice calculations and familiarize themselves with molecular weight determinations. It can be found on the diskette at the end of the book.

1.8. Steric Arrangement in Macromelecules

In linear polymers, due to the polymerization process, the pendant groups can be arranged into orderly configurations or they can lack such orderliness. Propylene, for instance, can be polymerized into two types of orderly steric arrangement. It can also be polymerized into one lacking steric order. The same can be true of other monosubstituted vinyl monomers. The steric arrangement in macromolecules is called *tacticity*. Polymers can be *isotactic*, where all the chiral centers have the same configuration (see Fig. 1.12). By picturing the chain backbone as drawn in the plane of the paper and by picturing all the phenyl groups as oriented above the plane -(Fig. 1.12a), isotactic polystyrene can then be visualized. The orderliness can also be of the type where every other chiral center has the same configuration. Such an arrangement is called *syndiotactic* (Fig. 1.12b). A lack of orderliness or randomness in the steric arrangement is called *atactic* or *heterotactic*. Stereospecific polymers can also be prepared from 1,2 disubstitued olefins. These macromolecules can be distereoisomers, or ditactic polymers. To describe the arrangement of such polymers, a *threo-erythro* terminology is used. An erythrodiisotactic polymer is one possessing alternating substituents - (-CHR'CHR-)-n. If we draw the carbon chain backbone in the plane of the paper, then all the R groups would find themselves on one side of the chain and all the R' groups on the other. They would, however, all be on the same side of the chain in a Fischer or in a Newman projection (Fig. 1.12c). A threo isomer or a threodiisotactic polymer can be illustrated in Fig. 1.12d.

Polymerization of 1,4-disubstituted butadienes can lead to products that possess two asymmetric carbon atoms and one double bond in each repeat unit. Such *tritactic* polymers are named with prefixes of *cis* or *trans* together with *erythro* or *threo* (see Fog. 1.13).

In polymers with single carbon to carbon bonds there is free rotation, if steric hindrance is absent. This allows the molecules to assume different spacial